

LIGAND DYNAMICS IN $\text{Mn}[\text{N}(\text{CN})_2]_2\text{-PYRAZINE}$

One of the major themes of solid state chemistry is the development of new molecular architectures with novel chemical and physical properties for applications such as chemical separation, catalysis, and magnetic devices. Compounds consisting of transition metal ions linked together by polydentate organic ligands are of particular interest because their properties can be tailored by judicious choice of the components. For example, changing the transition metal can alter both the bonding motif and magnetic properties of these systems. The properties of these materials can also be controlled by introducing ancillary π -conjugated ligands such as pyrazine (pyz), 4,4'-bipyridine and 2,2'-bipyridine. These molecular building blocks not only affect the spatial separation of the transition metal cations and the dimensionality of the crystal, but also modulate the superexchange interactions. For instance, of the many $\text{Mn}[\text{N}(\text{CN})_2]_2L$ materials examined to date, only $L = \text{pyrazine}$ exhibits long-range magnetic order above 2 K.

The structure of $\text{Mn}[\text{N}(\text{CN})_2]_2\text{-pyz}$ can be described as an inter-penetrating ReO_3 -like network with axially elongated Mn^{2+} octahedral and edges made-up of μ -bonded $[\text{N}(\text{CN})_2]^-$ anions and

neutral pyrazine ligands (Fig. 1) [1]. Upon heating above ≈ 200 K, Rietveld refinements of neutron powder diffraction (NPD) data indicate a marked increase in the Debye-Waller factor for the mid-nitrogen in the cyanamide ligand and a concomitant appearance of thermal diffuse scattering. Further heating to ≈ 400 K results in a phase transition to an unknown structure.

While the structural and magnetic behaviors of these materials have been rather well characterized, very little information has been obtained concerning the interactions that underlie the interesting bonding motifs. Due to its unique sensitivity to hydrogen and the possibility of covering a wide range of timescales, neutron spectroscopy is particularly well suited to probe ligand dynamics that directly reflect the bonding interactions. Quasielastic neutron scattering (QENS) provides information on the geometry and timescale of diffusive motions. For “localized” motions, the geometry is embodied in the elastic incoherent structure factor (EISF); the ratio of the elastic scattering to the total scattered intensity.

For all temperatures studied, a quasielastic signal due to the paramagnetic Mn^{2+} ions and the dynamics of the cyanamide ligand

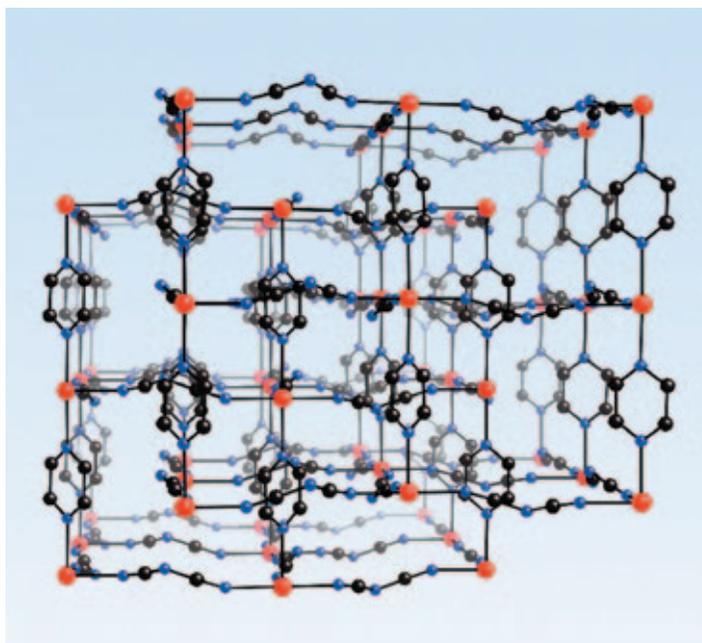


FIGURE 1. Crystal structure of $\text{Mn}[\text{N}(\text{CN})_2]_2\text{-pyz}$ showing the two independent, interpenetrating ReO_3 -like lattices. The hydrogen atoms of the pyrazine ring have been omitted, while the Mn, C, and N atoms are depicted as red, black, and blue spheres, respectively.

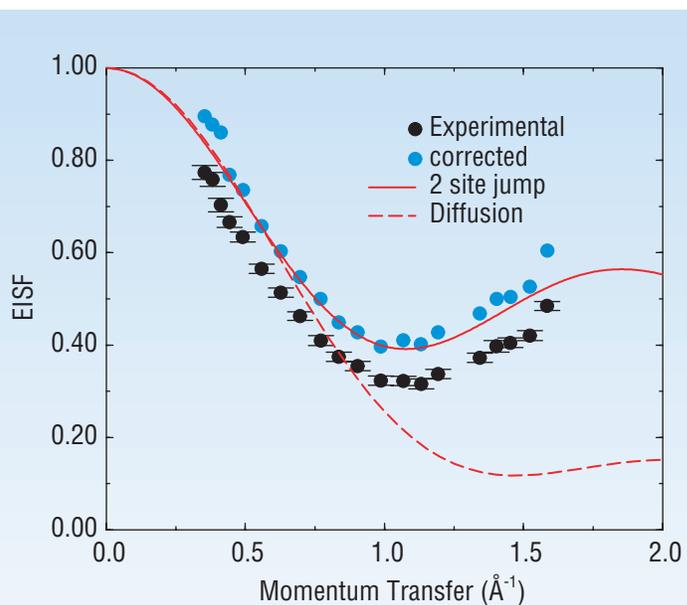


FIGURE 2. The experimental EISF (black circles) for $\text{Mn}[\text{N}(\text{CN})_2]_2\text{-pyz}$ at 425 K, has been corrected (blue circles) for coherent and paramagnetic quasielastic scattering. The solid red line is a fit to the corrected data with a 2-fold jump model that results in a proton jump distance of 4.17(1) Å. For comparison, the expected EISF for proton diffusion on a circle is also shown (red dashed line).

was observed. However, above ≈ 425 K, the quasielastic signal in the pyrazine compound is significantly larger. Figure 2 shows the Q -dependence of the EISF for the protonated compound and the same data after subtracting the measured quasielastic scattering from a deuterated material. These data are very well described by a two-fold proton jump model where the only variable parameter, the jump distance, is found to be $4.17(1)$ Å, consistent with the analysis of the NPD data which gives the D-D distance across the pyrazine ring as $\approx 4.16(2)$ Å. Further, the width of the quasielastic peak is constant over the entire Q -range, as expected for a simple, localized jump motion (the correlation time is ≈ 70 ps at 425 K). Thus, the pyrazine ligands must be performing π -jumps about the axis defined by the coordinating nitrogens.

The phonon density of states for $\text{Mn}[\text{N}(\text{CN})_2]_2\cdot\text{pyz}$ at selected temperatures covering all structural phases is shown in Fig. 3. In addition to the general broadening and softening of the spectral features with temperature, the intense peak assigned to the libration of the pyrazine ring at ≈ 11.2 meV is strongly attenuated and, assuming a two-fold cosine potential, suggests an activation energy

of ≈ 1.2 eV. Because this activation energy is much larger than $k_B T$ at the temperature where one observes fully dynamic pyrazines (425 K) and the quasielastic scattering appears abruptly at the structural transition, the transition must result in a greatly reduced rotational barrier. Unfortunately, the activation energy for this process was not measurable due to the proximity of the material's decomposition temperature.

Vibrational spectra at higher energy transfers were recorded on the FANS spectrometer (Fig. 4). Our calculations agree well with observation and show that the spectrum is dominated by the normal modes of the hydrogen containing pyrazine. Current investigations are aimed at understanding how the transition metal affects the dynamics of the ligands.

REFERENCES

- [1] J. L. Manson, Q.-Z. Huang, J. W. Lynn, H.-J. Koo, M.-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyriou, and J. S. Miller. Submitted to Journal of the American Chemical Society.

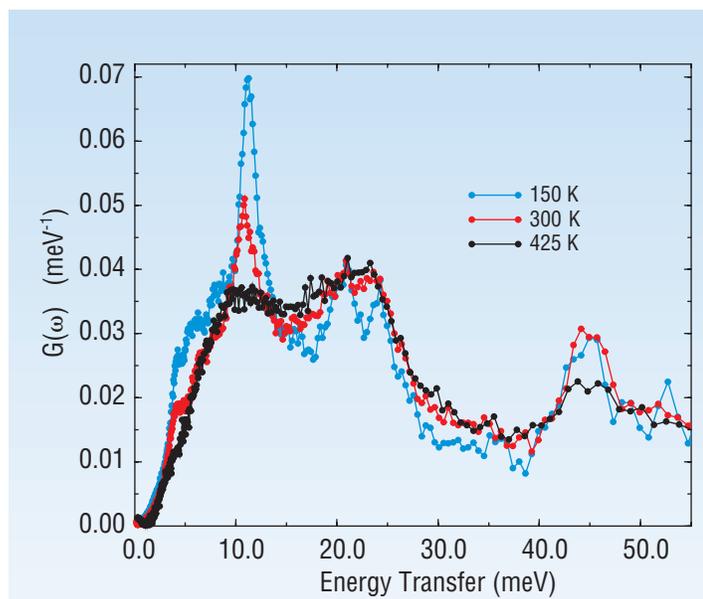


FIGURE 3. Temperature dependence of the vibrational density of states of $\text{Mn}[\text{N}(\text{CN})_2]_2\cdot\text{pyz}$ measured on the FCS spectrometer at a wavelength of 4.8 Å.

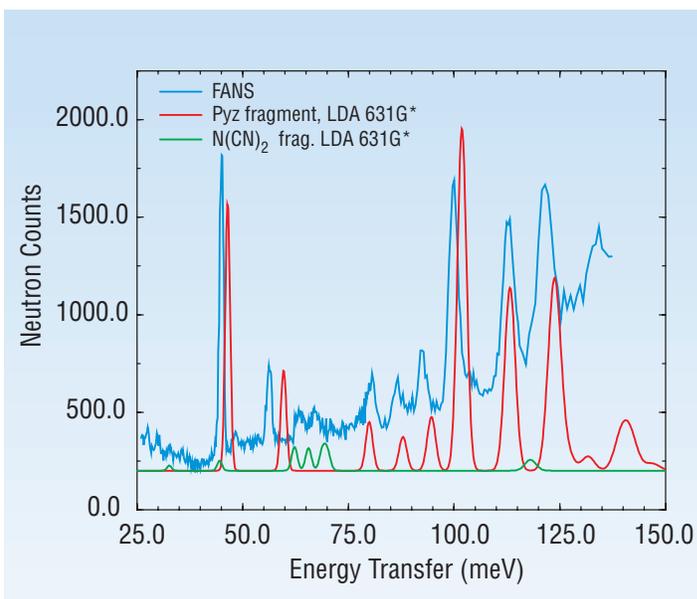


FIGURE 4. The vibrational spectrum (blue) of $\text{Mn}[\text{N}(\text{CN})_2]_2\cdot\text{pyz}$ (10 K) measured on the upgraded FANS spectrometer. Shown in red and green are the calculated contributions from chemically simplified, isolated fragments of $[\text{Ca-pyz-Ca}]^{4+}$ and $[\text{Ca-NCNCN-Ca}]^{3+}$, respectively.